

This Page Is Inserted by IFW Operations  
and is not a part of the Official Record

## **BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning documents *will not* correct images,  
please do not report the images to the  
Image Problem Mailbox.**

# PATENT SPECIFICATION

(11) 1 441 082

1 441 082

- (21) Application No. 21699/74 (22) Filed 16 May 1974  
 (31) Convention Application No. 2 326 100  
 (32) Filed 23 May 1973  
 (31) Convention Application No. 2 349 859  
 (32) Filed 4 Oct. 1973 in  
 (33) Germany (DT)  
 (44) Complete Specification published 30 June 1976  
 (51) INT CL<sup>2</sup> C03C 3/22  
 (52) Index at acceptance  
 C1M 11B3D1 11B3X 11C4 11C6 11C7 11C9 11J2 11J3  
 11K5 11K8 13E 13J 13S2A D27 S10B S10D S17A  
 S20



## (54) GLASS CERAMIC MATERIAL AND PROCESS FOR ITS PRODUCTION

(71)  
 6330  
 joint  
 of th  
 5 hereb  
 pray  
 and t  
 forme  
 by th  
 10 Th  
 ceram  
 tion  
 the a  
 as a l  
 15 Ma  
 osteo-  
 silver  
 the st  
 or c  
 20 mater  
 crylat

s, 45  
 it  
 1-  
 1-  
 s, 50  
 it  
 s.  
 ie  
 th  
 55  
 1-  
 1y  
 1-  
 1c 60  
 al  
 t,  
 e  
 1-  
 2. 65

### ERRATA

SPECIFICATION No. 1,441,082

Page 2, line 83, *delete* MgO *insert* MgO  
 Page 8, line 88, *delete* MgO *insert* MgO  
 Page 9, line 10, *delete* NaO<sub>2</sub> *read* Na<sub>2</sub>O

THE PATENT OFFICE  
 20th September, 1976

The compatibility of some of the above-mentioned implant materials in an animal or human organism may sometimes be regarded as satisfactory. However, none of the above-mentioned or other previously known or tested materials has been found to be of such quality as to grow together with the bones in a living organism.

30 The substance of animal or human bone consists substantially of hydroxylapatite, Ca<sub>3</sub> [(OH)(PO<sub>4</sub>)<sub>3</sub>], which forms an intermediate mixture with protein materials such as collagen. The very different chemical composition of bone replacement material and the bone itself is the reason why the previously known synthetic bone replacement materials have been found not to grow together with the bone mass.

40 At best, success may be achieved in reaching a certain mechanical anchoring by expedient profiling of the implant, the tissue near the bone simply enclosing the replacement material. The thus produced contact between

Under these conditions, the regeneration and the final construction of a load-bearing bone substitute might last for a rather long time. This time may be regarded as too long for practical purposes.

In an article under the title "Bonding mechanisms at the interface of ceramic prosthetic materials" by L. L. Hench, R. J. Splinter, T. K. Greenlee and W. C. Allen ("J. Biomed. Mater. Res. Symposium" No. 2 (Part 1). pp. 117—114 [1971]), it was proposed to employ as bone replacement material apatite-containing materials, which of themselves possess already a sufficient strength, so that, after growing in, a full loadability is immediately achieved. There are proposed in this article glass ceramic materials in which, by suitable thermal treatment, apatite grains are generated in a sufficient number for bone growth to take place, for example, in known manner. In this process, it may be regarded as certain that this material can grow together with the bone *in situ*.

# PATENT SPECIFICATION

(11) 1 441 082

1 441 082

- (21) Application No. 21699/74 (22) Filed 16 May 1974  
 (31) Convention Application No. 2 326 100  
 (32) Filed 23 May 1973  
 (31) Convention Application No. 2 349 859  
 (32) Filed 4 Oct. 1973 in  
 (33) Germany (DT)  
 (44) Complete Specification published 30 June 1976  
 (51) INT CL<sup>2</sup> C03C 3/22  
 (52) Index at acceptance  
 C1M 11B3D1 11B3X 11C4 11C6 11C7 11C9 11J2 11J3  
 11K5 11K8 13E 13J 13S2A D27 S10B S10D S17A  
 S20



## (54) GLASS CERAMIC MATERIAL AND PROCESS FOR ITS PRODUCTION

(71) We, ERNST LEITZ GMBH, of 6330 Wetzlar, German Federal Republic, a joint stock company organised under the laws of the Federal Republic of Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a glass ceramic material, to a process for the production of the glass ceramic material and to the application of the material, for example as a bone replacement material.

Materials used in bone plastic surgery and osteo-synthesis include metals, for example silver and tantalum, metal alloys, for example the surgical fine steel known as "vitallium" or chromium-cobalt alloy, and synthetic materials, for example polyethylene, methacrylates or silicone rubber.

The compatibility of some of the above-mentioned implant materials in an animal or human organism may sometimes be regarded as satisfactory. However, none of the above-mentioned or other previously known or tested materials has been found to be of such quality as to grow together with the bones in a living organism.

The substance of animal or human bone consists substantially of hydroxylapatite,  $\text{Ca}_3 [(\text{OH})(\text{PO}_3)_2]$ , which forms an intermediate mixture with protein materials such as collagen. The very different chemical composition of bone replacement material and the bone itself is the reason why the previously known synthetic bone replacement materials have been found not to grow together with the bone mass.

At best, success may be achieved in reaching a certain mechanical anchoring by expedient profiling of the implant, the tissue near the bone simply enclosing the replacement material. The thus produced contact between

the synthetic implant and the bone remains, however, rather weak, and generally cannot be exposed to normal loadings.

It is already known to start from the mineral hydroxyl-apatite in attempting to regenerate bone substances. In such a process, this substance acts as an attachment point for the protein material of the bone mass. Starting from apatite grains, a complete bone is built up. Simultaneously, by means of such a process connections to bone fragments which are still present are produced (callus formation).

In principle it would be possible to employ apatite in sintered form as a bone replacement material. However, this might have the difficulty that to achieve a sufficient initial stability of the prosthesis or prosthesis part, very large quantities of apatite might have to be employed, far in excess of the quantities required for the construction of a bone. Under these conditions, the regeneration and the final construction of a load-bearing bone substitute might last for a rather long time. This time may be regarded as too long for practical purposes.

In an article under the title "Bonding mechanisms at the interface of ceramic prosthetic materials" by L. L. Hench, R. J. Splinter, T. K. Greenlee and W. C. Allen ("J. Biomed. Mater. Res. Symposium" No. 2 (Part 1), pp. 117—114 [1971]), it was proposed to employ as bone replacement material apatite-containing materials, which of themselves possess already a sufficient strength, so that, after growing in, a full loadability is immediately achieved. There are proposed in this article glass ceramic materials in which, by suitable thermal treatment, apatite grains are generated in a sufficient number for bone growth to take place, for example, in known manner. In this process, it may be regarded as certain that this material can grow together with the bone *in situ*.

SEE ERRATA SLIP ATTACHED

The glass ceramic materials proposed by Hench *et al* may, however, possess important difficulties, which may cause their application in an animal or human organism — in particular in the case of larger prostheses — to become a severe risk to the implant carrier.

Since the ratio of the two ions  $\text{Na}^+$  and  $\text{K}^+$  to one another is of decisive importance for the operation of the nerves and muscles in an animal organism, even relatively small shifts of, in particular, the potassium ion concentration can alter the excitability of the nerves and thus lead to severe heart injury. This ion ratio is so much the more significant because the extra-cellular potassium ion concentration, which may be regarded as a very significant quantity, makes up only about 2% of the total potassium content of an organism. Disturbances in this small extra-cellular material, comprising as a whole only about 2 to 3 grams of  $\text{K}^+$  ions, can be generated even by relatively small shifts in the potassium content of the blood or of the lymph.

Similar considerations apply to the ions  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ , which are also present in an animal or human organism in an invariable ratio and in a similarly invariable concentration, the shifting of which generates severe injury in the pertaining organisms.

The glass ceramic materials proposed by Hench *et al* are produced from pure sodium-calcium-glasses. It is self-evident that, as regards the known capability of the glasses to act as ion exchangers, a potential of  $\text{Na}^+$  and  $\text{Ca}^{2+}$  ions is present which, on the one hand, strongly alters the concentration of these two ions in the surroundings of the glass ceramic implant by simple extraction and, on the other hand, considerably reduces the concentration of the antagonist ions, for example  $\text{K}^+$  and  $\text{Mg}^{2+}$ , by exchange adsorption. It is thus to be expected that in the case of larger prostheses the effect on the respective ion concentration is extended, in dependence upon geometrical shape, to other organs and the operation thereof. In particular, a high shift of the ion ratio, which is particularly favourable on medicine technology grounds, is to be expected when the ceramic materials are employed in the form of porous sintered or foam materials.

A further difficulty with the known glass ceramic materials is their relatively small nucleation tendency. This may lead to extremely long and technically expensive recrystallisation processes. Moreover, the number of formed nuclei per unit volume is technically difficult to control, since it is dependent upon many imponderables, such as the degree of purity of the chemical starting substances, prior heat treatment of the glass, the material of the melting crucible, the constancy of the heat travel and so on.

According to one aspect of the present in-

vention, there is provided a glass ceramic material comprising

20 to 60 weight %	$\text{SiO}_2$ ,	65
5 to 40 weight %	$\text{P}_2\text{O}_5$ ,	
2.7 to 20 weight %	$\text{Na}_2\text{O}$ ,	
0.4 to 20 weight %	$\text{K}_2\text{O}$ ,	70
2.9 to 30 weight %	$\text{MgO}$ , and	
5 to 40 weight %	$\text{CaO}$ ,	

the balance, if any, consisting of other compatible non-toxic constituents and impurities.

Preferably, the balance comprises 0.05 to 3 weight %  $\text{F}_2$  in the form of a fluoride or fluoride compound.

Preferably, also, the material comprises

30 to 60 weight %	$\text{SiO}_2$ ,	80
5 to 20 weight %	$\text{P}_2\text{O}_5$ ,	
3 to 10 weight %	$\text{Na}_2\text{O}$ ,	
3 to 10 weight %	$\text{K}_2\text{O}$ ,	
5 to 20 weight %	$\text{MgO}$ , and	
10 to 30 weight %	$\text{CaO}$ ,	

the balance expediently comprising 0.5 to 2.5 weight %  $\text{F}_2$  in the form of a fluoride or fluoride compound.

Suitably  $\text{Na}^+$  and  $\text{K}^+$  ions are inhomogeneously distributed, and preferably the surface concentration of  $\text{K}^+$  ions is greater than the overall  $\text{K}^+$  ion concentration, and the surface concentration of  $\text{Na}^+$  ions is less than the overall  $\text{Na}^+$  ion concentration.

According to a second aspect of the present invention, there is provided a process for the production of a glass ceramic material, comprising the step of melting a batch comprising  $\text{SiO}_2$ ,  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ ,  $\text{MgO}$ , and a calcium phosphate compound, the proportions of the components of the batch being so selected as to produce a material according to the first aspect of the invention.

Preferably the batch further comprises  $\text{F}_2$  in the form of a fluoride or fluoride compound, the proportions of the components of the batch being so selected as to produce a material according to the first aspect of the invention.

Conveniently, the batch comprises

20 to 60 weight %	$\text{SiO}_2$ ,	110
2.7 to 20 weight %	$\text{Na}_2\text{O}$ ,	
0.4 to 20 weight %	$\text{K}_2\text{O}$ ,	
2.9 to 30 weight %	$\text{MgO}$ ,	
5 to 25 weight %	$\text{CaO}$ , and	
10 to 30 weight %	$\text{Ca}_3(\text{PO}_4)_2$ ,	115

the batch being subjected in succession to the following steps:

- (a) heating to a first temperature in the range of  $550^\circ\text{C}$  to  $950^\circ\text{C}$ ,
- (b) maintenance of the first temperature for from 8 to 30 hours,

- (c) cooling to a second temperature in the range of 350°C to 550°C,  
 (d) maintenance of the second temperature for from 2 to 5 hours,  
 5 (e) heating to a third temperature in the range of 700°C to 1150°C,  
 (f) maintenance of the third temperature for from 10 to 40 hours, and  
 (g) cooling to room temperature.
- 10 If so desired, the 10 to 30 weight %  $\text{Ca}_3(\text{PO}_4)_2$  may be replaced by up to 25 weight %  $\text{Ca}(\text{PO}_3)_2$ .  
 Conveniently, the batch further comprises up to 5 weight %  $\text{CaF}_2$ .
- 15 The batch may comprise
- |    |   |  |
|----|---|--|
|    | 30 to 60 weight % $\text{SiO}_2$ ,                |  |
|    | 3 to 10 weight % $\text{Na}_2\text{O}$ ,          |  |
|    | 3 to 10 weight % $\text{K}_2\text{O}$ ,           |  |
|    | 5 to 20 weight % $\text{MgO}$ ,                   |  |
| 20 | 10 to 20 weight % $\text{CaO}$ , and              |  |
|    | 20 to 30 weight % $\text{Ca}_3(\text{PO}_4)_2$ or |  |
|    | 10 to 20 weight % $\text{Ca}(\text{PO}_3)_2$ .    |  |
- The batch may comprise
- |    |  |  |
|----|--|--|
| 25 | 38.0 to 47.3 weight % $\text{SiO}_2$ ,               |  |
|    | 2.7 to 12.0 weight % $\text{Na}_2\text{O}$ ,         |  |
|    | 0.4 to 6.8 weight % $\text{K}_2\text{O}$ ,           |  |
|    | 2.9 to 16.5 weight % $\text{MgO}$ ,                  |  |
|    | 10.0 to 23.6 weight % $\text{CaO}$ ,                 |  |
| 30 | up to 25.5 weight % $\text{Ca}_3(\text{PO}_4)_2$ or  |  |
|    | up to 18.4 weight % $\text{Ca}(\text{PO}_3)_2$ , and |  |
|    | up to 4.0 weight % $\text{CaF}_2$ .                  |  |
- The batch may also comprise at least one further compound yielding fluoride ions, or the
- 35  $\text{CaF}_2$  may be replaced by at least one further compound yielding fluoride ions.
- The process may comprise the step of subjecting the batch to such a heat treatment as to produce a gradient in the size and number of crystallites formed in the material.
- 40 According to a third aspect of the present invention, there is provided a process for the production of a glass ceramic material, comprising the steps of melting a batch comprising  $\text{SiO}_2$ ,  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ ,  $\text{MgO}$ ,  $\text{CaF}_2$  and a calcium phosphate compound, the proportions of the components of the batch being so selected as to form by said melting an intermediate product having a  $\text{K}^+$  ion content less
- 45 than that of the desired glass ceramic material, cooling the intermediate product, and subjecting said cooled intermediate product in succession to the following steps:
- |    |   |    |
|----|---|----|
| 55 | (a) heating to a first temperature in the range of 550°C to 950°C,            |    |
|    | (b) maintenance of the first temperature for from 8 to 30 hours,              |    |
|    | (c) cooling to a second temperature in the range of 350°C to 550°C,           |    |
|    | (d) maintenance of the second temperature for from 2 to 5 hours,              |    |
|    | (e) heating to a third temperature in the range of 700°C to 1150°C,           |    |
|    | (f) maintenance of the third temperature for from 10 to 40 hours,             |    |
|    | (g) cooling to room temperature, and  |    |
|    | (h) introduction of $\text{K}^+$ ions to produce a material as defined above. | 60 |
- According to a fourth aspect of the present invention, there is provided a process for the production of a glass ceramic material, comprising the steps of melting a batch comprising  $\text{SiO}_2$ ,  $\text{Na}_2\text{O}$ ,  $\text{MgO}$ ,  $\text{CaF}_2$  and a calcium phosphate compound, the proportions of the components of the batch being so selected as to form by said melting an intermediate product free of  $\text{K}^+$  ions, cooling the intermediate product, and subjecting said cooled intermediate product in succession to the following steps:
- |    |   |    |
|----|---|----|
| 70 | (a) heating to a first temperature in the range of 550°C to 950°C,            |    |
|    | (b) maintenance of the first temperature for from 8 to 30 hours,              |    |
|    | (c) cooling to a second temperature in the range of 350°C to 550°C,           |    |
|    | (d) maintenance of the second temperature for from 2 to 5 hours,              |    |
|    | (e) heating to a third temperature in the range of 700°C to 1150°C,           |    |
|    | (f) maintenance of the third temperature for from 10 to 40 hours,             |    |
|    | (g) cooling to room temperature, and  |    |
|    | (h) introduction of $\text{K}^+$ ions to produce a material as defined above. | 75 |
- The introduction step may take place by ion implantation, or by treating the intermediate product with a fused salt bath containing  $\text{K}^+$  ions, the salt bath preferably comprising  $\text{KNO}_3$ . The salt bath may be at a temperature in the range of 360°C to 480°C, preferably 400°C, and the treating step may have a duration of from 2 to 4 hours, preferably 3 hours.
- 80
- A bone replacement glass ceramic material as defined above may be found not to possess the difficulties shown by prior bone replacement materials, and furthermore may exhibit the apatite structure favourable for the intimate growing together and also a distinctively good organ compatibility.
- 85
- Some examples of materials according to the present invention will be described below with reference to the following Tables and Figures of the accompanying drawings.
- 90
- A glass with a composition indicated in Example 1 in Table 1 is crystallized and subsequently cooked for 6.5 hours in a reflux condenser in a Ringer's solution. The solution is made as follows: A tablet consisting of
- 95
- 100
- 105
- 110
- 115
- 120

- variation of the above-mentioned ion ratio in the initial composition of the glass ceramic material, a value, optimally desired for the organism, can be achieved in the solution. Similar considerations apply to the  $\text{Ca}^{2+}/\text{Mg}^{2+}$  ratio; however, in this case further ion exchange processes have to be considered.
- As a result of this treatment it was found that it is possible to melt glasses which show apatite structure in crystallisation, but which, in the case of extraction in Ringer's solution, yield  $\text{Na}^+$  and  $\text{K}^+$  ions or  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions in the desired ratio.
- In the following Table 1, batch compositions according to the present invention are given by way of example.

TABLE 1 (Weight %)

Batch Number	1	2	3	4	5	6	7	8	9	10	11
$\text{SiO}_2$	46.2	43.0	45.6	46.5	47.3	43.0	43.0	43.0	43.0	43.0	43.0
$\text{Ca}_3(\text{PO}_4)_2$	25.5	21.0	22.3	22.7	23.2	21.0	21.0	21.0	21.0	21.0	21.0
$\text{CaO}$	20.2	16.0	16.0	16.0	16.0	15.0	14.0	13.0	12.0	11.8	11.0
$\text{MgO}$	2.9	7.0	7.0	7.0	7.0	8.0	9.0	10.0	11.0	11.5	12.0
$\text{Na}_2\text{O}$	4.8	12.0	8.4	7.2	6.0	12.0	12.0	12.0	12.0	5.9	12.0
$\text{K}_2\text{O}$	0.4	1.0	0.7	0.6	0.5	1.0	1.0	1.0	1.0	6.8	1.0

The controlled crystallisation of the apatite structure in the material is favoured in particular by the addition of calcium fluoride ( $\text{CaF}_2$ ).  
 Tables 2 shows examples of batch compositions, which additionally contain  $\text{CaF}_2$  and in which the calcium phosphate compound is either  $\text{Ca}_3(\text{PO}_4)_2$  or  $\text{Ca}(\text{PO}_3)_2$ . It is also possible to provide batch compositions, which contain the above-mentioned calcium phosphate compounds together in the same composition.

5

TABLE 2 (Weight %)

Batch Number	12	13	14	15	16	17	18	19	20	21	22	23
$\text{SiO}_2$	43.0	38.0	38.0	38.0	46.0	43.0	43.0	43.0	46.0	43.0	43.0	43.0
$\text{Ca}_3(\text{PO}_4)_2$	—	—	—	—	—	—	—	—	—	—	21.0	21.0
$\text{Ca}(\text{PO}_3)_2$	13.4	18.4	13.4	13.4	13.4	16.4	13.4	13.4	13.4	13.4	—	—
$\text{CaO}$	18.6	18.6	18.6	23.6	18.6	18.6	18.6	21.6	18.6	18.6	11.0	10.0
$\text{MgO}$	11.5	11.5	16.5	11.5	11.5	11.5	14.5	11.5	11.5	11.5	11.5	10.5
$\text{Na}_2\text{O}$	5.7	5.7	5.7	5.7	2.7	2.7	2.7	2.7	5.7	5.7	5.7	5.7
$\text{K}_2\text{O}$	6.8	6.8	6.8	6.8	6.8	6.8	6.8	6.8	3.8	3.8	6.8	6.8
$\text{CaF}_2$	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	4.0	1.0	3.0

In the case of the addition of  $\text{CaF}_2$ , the nucleation action may be represented diagrammatically with reference to some batch composition examples.

In the following grouping in Table 3, three examples are represented, which have already been set out in the two preceding Tables 1 and 2.

TABLE 3 (Weight %)

	from Table 1 Batch No. 10	from Table 2	
		Batch No. 22	Batch No. 23
Number in Fig. 2	I	II	III
$\text{SiO}_2$	43.0	43.0	43.0
$\text{Ca}_3(\text{PO}_4)_2$	21.0	21.0	21.0
$\text{CaO}$	11.8	11.0	10.0
$\text{MgO}$	11.5	11.5	10.5
$\text{Na}_2\text{O}$	5.9	5.7	5.7
$\text{K}_2\text{O}$	6.8	6.8	6.8
$\text{CaF}_2$	—	1.0	3.0
radio-graphically determined component	very weak crystallisation: crystals not identifiable	clear crystallisation of apatite	very strong crystallisation of apatite

- 10 In Fig. 2, a bar graph is indicated in schematic representation for radiographic diffractometer recordings of glass ceramic materials, which are melted from the batch examples listed in Table 3 under I to III.
- 15 The respective height of the discrete lines is a measure of the relative intensity of the pertaining peak, and this again is a measure of the degree of crystallinity of the respective mineral component. Thus in Fig. 2, the angle of incidence  $\theta$  is plotted on the abscissa, and the relative intensity on the ordinate of each part of the graph. The radiographic recordings were carried out under the following conditions:

- 25 röntgen radiation:  $\text{CuK}_\alpha$   
wavelength: 1.5418 Angstrom units  
filter: Ni  
voltage: 40 kilovolts.

- 30 Within a  $\theta$ -interval of  $23^\circ$  to  $34^\circ$  ( $\theta$  being the Bragg reflection angle or angle of incidence), all characteristic peaks occurred. The diagrams could be identified with the aid

of the ASTM-card index system.

In the upper part I of Fig. 2, only three lines of weak intensity are indicated, which do not permit a reliable determination of the substance. While example I had no  $\text{CaF}_2$  addition, in the middle part II of Fig. 2 there is plotted a material which contains 1 weight %  $\text{CaF}_2$  and was subjected to the same temperature-time treatment program as example I. There occur characteristic lines, which permit identification as apatite. Finally, example III shows a recording of a material melted from a batch, which contains *inter alia* 3 weight %  $\text{CaF}_2$ . The marked diffractometer diagram clearly makes possible a conclusion on the presence of the mineral component apatite. Thus, it is clearly established that the addition of a fluoride — in particular  $\text{CaF}_2$  — to the batch with maintenance of a specific temperature-time treatment program leads to a crystal phase with apatite structure in the glass ceramic matrix. In Table 4, the evaluation result of the diagrams represented in Fig. 2 is indicated.



TABLE 4

Bragg angle (°)	d-values (Å)	indices (hkl)	designation of the component	ASTM-card index number
33.4	2.68	300	Carbonate-apatite (dahlite)	13 - 1
33.3	2.69	300	Carbonate-apatite	19 - 272
32.3	2.77	142	Carbonate-apatite (dahlite)	13 - 1
32.2	2.78	211/112	Carbonate-apatite	19 - 272
28.8	3.07	001	CaO.SiO <sub>2</sub>	9 - 210
26.2	3.40	002	Carbonate-apatite	19 - 272
23.4	3.80	—	Nagelschmidtite	5 - 0646

It should be emphasised that the identification of the indicated mineral component verifies the general, crystallographically-based statement that in the investigated material samples there is involved the formation of an apatite crystal lattice structure, since isotropy or at least iso-type relationships are present between the carbonate apatite with the mineral name dahlite (ASTM-card index No. 13—1) or the carbonate apatite (ASTM-card index No. 19—272) and, for example, the hydroxyl-apatite or the fluorine apatite.

In Fig. 3, the temperature-time program optimal for a process according to the invention is illustrated schematically. The abbreviations used in this Figure have the following meanings:

$T_{KN}$ : temperature of maximal crystal formation speed;

$T_{KW}$ : temperature of maximal crystal growth speed;

$T_0$ : setting temperature.

The following ranges apply to the individual temperature and time indications:

$T_{KN}$ : 550°C to 950°C

$T_{KW}$ : 700°C to 1150°C

$T_0$ : 350°C to 550°C

$t_1$ : 8 to 30 hours

$t_2$ : 2 to 5 hours

$t_3$ : 10 to 40 hours.

The melting process for an embodiment is described below. Firstly there takes place the melting of a batch situated, for example, in a platinum crucible, at about 1480°C for a period of time of about 3 to 4 hours. Thereafter, there takes place normal cooling to room temperature or there follows the tem-

perature program represented graphically in Fig. 3 for the generation of a glass ceramic material containing apatite structure.

It should be emphasised that the addition of subordinate components of B<sub>2</sub>O<sub>3</sub> or other substances conventional in general in the glass technology, with the exception of toxicologically active compounds (for example, BeO and PbO), also lies within the scope of the present invention.

An increase in the mechanical strength of this glass ceramic material, substantially with maintenance of its other properties, may be achieved if instead of a quasi-homogeneous distribution of its individual ionic components — in particular Na<sup>+</sup> and K<sup>+</sup> ions — the material has an inhomogeneous distribution of the Na<sup>+</sup> and K<sup>+</sup> ions.

The K<sup>+</sup> ion concentration in the surface region of the material can be higher than the overall K<sup>+</sup> ion concentration of the material, and the Na<sup>+</sup> ion concentration in the surface region of the material can be lower than the overall Na<sup>+</sup> ion concentration of the material. If this is so, then there results a surface region of the material standing under pressure stress, which region is harder than the core of the material. A glass according to the invention with such an ion concentration "profile" may show advantages for some purposes.

Fig. 4 shows in a graphical representation the dependence of the sample number upon the measured elasticity modulus. In Fig. 4, the elasticity modulus in kiloponds per square millimetre is plotted on the abscissa, and the sample number on the ordinate. The measurement values designated by the circular symbols were obtained in the examination of samples which had a homogeneous distribution of the Na<sup>+</sup> and K<sup>+</sup> ions (curve I). The

square symbols designate those measurement values which were obtained with material samples with inhomogeneous distribution of their Na<sup>+</sup> and K<sup>+</sup> ions (curve II). A comparison of the measurement values according to position and absolute height shows clearly that the maximum of the distribution of the elasticity moduli in the case of curve II is clearly displaced towards higher values.

10 The above-described variant of the process will now be described with reference to an example. From a batch of the composition

15 43 weight % SiO<sub>2</sub>  
21 weight % Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>  
11 weight % CaO  
11 weight % MgO  
10 weight % Na<sub>2</sub>O  
2 weight % CaF<sub>2</sub> and  
2 weight % K<sub>2</sub>O

20 a vitreous intermediate product is melted at a temperature of 1480°C for a melting time of 3 hours. After cooling to room temperature, this intermediate product is heated to 820°C, held at this temperature for 10 hours, cooled to 550°C and left for two hours at this temperature. It is then further heated to 920°C and held at this temperature for 36 hours. The thus obtained intermediate product is thereafter hardened by dipping in a KNO<sub>3</sub> melt at 400°C for 3 hours.

30 A wet extraction with Ringer's solution in the above-described manner achieves a value of 16 for the ratio Na<sup>+</sup>/K<sup>+</sup>. It is evident that by alteration of the dipping time of the intermediate product in the salt melt, this ratio can be increased or decreased. The intermediate product can also be subjected to an ion implantation. Such material transport of solid physical bodies is known as such and thus is not further described.

40 The application of the thus produced glass ceramic materials as a partial or complete replacement material or filler for bones or teeth is, besides the already mentioned properties such as organ compatibility and ability to grow together with the bone situated in an organism, particularly expedient because these materials may readily be worked and reworked mechanically. These glass ceramic materials are castable in moulds, and are plastically deformable. They can also be pressed, cut, blown, milled, sawed, filed and bored. When in the form of a porous sintered or foam material, the material has a very large specific surface area. These materials can be provided with dispersively inserted pigments or colourings for certain decorative purposes. In addition, it is possible to optimise the solid body mechanical parameters by controlled inlays in the manner of the fibre-reinforced materials. Finally, the implants can be prepared, without mechanical stability losses, in the form of tubes, which enables

a considerable saving of material and thus also of weight. In this manner the economic production of, for example, implants may be made possible.

#### WHAT WE CLAIM IS:—

1. A glass ceramic material comprising

20 to 60 weight % SiO<sub>2</sub>, 70  
5 to 40 weight % P<sub>2</sub>O<sub>5</sub>,  
2.7 to 20 weight % Na<sub>2</sub>O,  
0.4 to 20 weight % K<sub>2</sub>O,  
2.9 to 30 weight % MgO, and  
5 to 40 weight % CaO, 75

the balance, if any, consisting of other compatible non-toxic constituents and impurities.

2. A material as claimed in claim 1, wherein the balance comprises 0.05 to 3 weight % F<sub>2</sub> in the form of a fluoride or fluoride compound. 80

3. A material as claimed in claim 1, comprising

30 to 60 weight % SiO<sub>2</sub>,  
5 to 20 weight % P<sub>2</sub>O<sub>5</sub>, 85  
3 to 10 weight % Na<sub>2</sub>O,  
3 to 10 weight % K<sub>2</sub>O,  
5 to 20 weight % MgO, and  
10 to 30 weight % CaO,

4. A material as claimed in claim 3, wherein the balance comprises 0.5 to 2.5 weight % F<sub>2</sub> in the form of a fluoride or fluoride compound. 90

5. A material as claimed in any one of the preceding claims, wherein Na<sup>+</sup> and K<sup>+</sup> ions are inhomogeneously distributed. 95

6. A material as claimed in claim 5, wherein the surface concentration of K<sup>+</sup> ions is greater than the overall K<sup>+</sup> ion concentration, and the surface concentration of Na<sup>+</sup> ions is less than the overall Na<sup>+</sup> ion concentration. 100

7. A glass ceramic material substantially as hereinbefore described with reference to any one of the compositions numbered 1 to 23.

8. A process for the production of a glass ceramic material, comprising the step of melting a batch comprising SiO<sub>2</sub>, Na<sub>2</sub>O, K<sub>2</sub>O, MgO and a calcium phosphate compound, the proportions of the components of the batch being so selected as to produce a material as claimed in claim 1. 105

9. A process as claimed in claim 8, wherein the batch further comprises F<sub>2</sub> in the form of a fluoride or fluoride compound, the proportions of the components of the batch being so selected as to produce a material as claimed in claim 2. 110

10. A process for the production of a glass ceramic material, comprising the step of melting a batch comprising SiO<sub>2</sub>, Na<sub>2</sub>O, K<sub>2</sub>O, MgO and a calcium phosphate compound, the proportions of the components of the batch being so selected as to produce a material as claimed in claim 3. 115

11. A process as claimed in claim 10, wherein the batch further comprises  $F_2$  in the form of a fluoride or fluoride compound, the proportions of the components of the batch being so selected as to produce a material as claimed in claim 4.

12. A process as claimed in claim 8, wherein the batch comprises

- 20 20 to 60 weight %  $SiO_2$ ,  
 2.7 to 20 weight %  $Na_2O$ ,  
 0.4 to 20 weight %  $K_2O$ ,  
 2.9 to 30 weight %  $MgO$ ,  
 5 to 25 weight %  $CaO$ , and  
 15 10 to 30 weight %  $Ca_3(PO_4)_2$ ,  
 or  
 up to 25 weight %  $Ca(PO_3)_2$ .

the batch being subjected in succession to the following steps:

- 20 (a) heating to a first temperature in the range of  $550^\circ C$  to  $950^\circ C$ ,  
 (b) maintenance of the first temperature for from 8 to 30 hours,  
 (c) cooling to a second temperature in the range of  $350^\circ C$  to  $550^\circ C$ ,  
 25 (d) maintenance of the second temperature for from 2 to 5 hours,  
 (e) heating to a third temperature in the range of  $700^\circ C$  to  $1150^\circ C$ ,  
 (f) maintenance of the third temperature for from 10 to 40 hours, and  
 30 (g) cooling to room temperature.

13. A process as claimed in claim 12, wherein the batch further comprises up to 5 weight %  $CaF_2$  and/or at least one further compound yielding fluoride ions.

14. A process as claimed in claim 12, wherein the batch comprises

- 40 30 to 60 weight %  $SiO_2$ ,  
 3 to 10 weight %  $Na_2O$ ,  
 3 to 10 weight %  $K_2O$ ,  
 5 to 20 weight %  $MgO$ ,  
 10 to 20 weight %  $CaO$ , and  
 20 to 30 weight %  $Ca_3(PO_4)_2$  or  
 10 to 20 weight %  $Ca(PO_3)_2$ .

15. A process as claimed in claim 8, wherein the batch comprises

- 50 38.0 to 47.3 weight %  $SiO_2$ ,  
 2.7 to 12.0 weight %  $Na_2O$ ,  
 0.4 to 6.8 weight %  $K_2O$ ,  
 2.9 to 16.5 weight %  $MgO$ ,  
 10.0 to 23.6 weight %  $CaO$ ,  
 up to 25.5 weight %  $Ca_3(PO_4)_2$  or  
 up to 18.4 weight %  $Ca(PO_3)_2$ ,  
 and  
 55 up to 4.0 weight %  $CaF_2$ .  
 and/or

at least one further compound yielding fluoride ions.

16. A process as claimed in any one of claims 8 to 15, comprising the step of subjecting the batch to such a heat treatment as to produce a gradient in the size and number of crystallites formed in the material.

17. A process for the production of a glass ceramic material, comprising the steps of melting a batch comprising  $SiO_2$ ,  $Na_2O$ ,  $K_2O$ ,  $MgO$ ,  $CaF_2$  and a calcium phosphate compound, the proportions of the components of the batch being so selected as to form by said melting an intermediate product having a  $K^+$  ion content less than that of the desired glass ceramic material, cooling the intermediate product, and subjecting said cooled intermediate product in succession to the following steps:

- (a) heating to a first temperature in the range of  $550^\circ C$  to  $950^\circ C$ ,  
 (b) maintenance of the first temperature for from 8 to 30 hours,  
 (c) cooling to a second temperature in the range of  $350^\circ C$  to  $550^\circ C$ ,  
 (d) maintenance of the second temperature for from 2 to 5 hours,  
 (e) heating to a third temperature in the range of  $700^\circ C$  to  $1150^\circ C$ ,  
 (f) maintenance of the third temperature for from 10 to 40 hours,  
 (g) cooling to room temperature, and  
 (h) introduction of further  $K^+$  ions to produce a material as claimed in claim 1.

18. A process for the production of a glass ceramic material, comprising the steps of melting a batch comprising  $SiO_2$ ,  $Na_2O$ ,  $MgO$ ,  $CaF_2$  and a calcium phosphate compound, the proportions of the components of the batch being so selected as to form by said melting an intermediate product free of  $K^+$  ions, cooling the intermediate product, and subjecting said cooled intermediate product in succession to the following steps:

- (a) heating to a first temperature in the range of  $550^\circ C$  to  $950^\circ C$ ,  
 (b) maintenance of the first temperature for from 8 to 30 hours,  
 (c) cooling to a second temperature in the range of  $350^\circ C$  to  $550^\circ C$ ,  
 (d) maintenance of the second temperature for from 2 to 5 hours,  
 (e) heating to a third temperature in the range of  $700^\circ C$  to  $1150^\circ C$ ,  
 (f) maintenance of the third temperature for from 10 to 40 hours,  
 (g) cooling to room temperature, and  
 (h) introduction of  $K^+$  ions to produce a material as claimed in claim 1.

19. A process as claimed in either claim 17 or claim 18, wherein said introduction step takes place by ion implantation.

20. A process as claimed in either claim 17 or claim 18, wherein said introduction step comprises the step of treating the intermediate

product with a fused salt bath containing K<sup>+</sup> ions.

21. A process as claimed in claim 20, wherein the salt bath comprises KNO<sub>3</sub>.

5 22. A process as claimed in either claim 20 or claim 21, wherein the salt bath is at a temperature in the range of 360°C to 480°C, and said treating step has a duration of from 2 to 4 hours.

10 23. A process as claimed in claim 22, wherein the salt bath is at a temperature of 400°C, and said treating step has a duration of 3 hours.

15 24. A process for the production of a glass ceramic material, substantially as hereinbefore described with reference to any one of Compositions 1 to 23.

25. A glass ceramic material produced by

a process as claimed in any one of claims 8 to 24.

26. A surgical or dental prosthesis constructed of a glass ceramic material as claimed in any one of claims 1 to 7 and 25.

27. A porous substance sintered from a material as claimed in any one of claims 1 25 to 7 and 25.

28. A filler comprising a glass ceramic material as claimed in any one of claims 1 to 7 and 25.

DR. WALTHER WOLFF & CO.,  
75, Victoria Street,  
London, S.W.1.  
Chartered Patent Agents,  
Agents for the Applicants.

1441082

COMPLETE SPECIFICATION

3 SHEETS

This drawing is a reproduction of  
the Original on a reduced scale

Sheet 1

Fig. 1

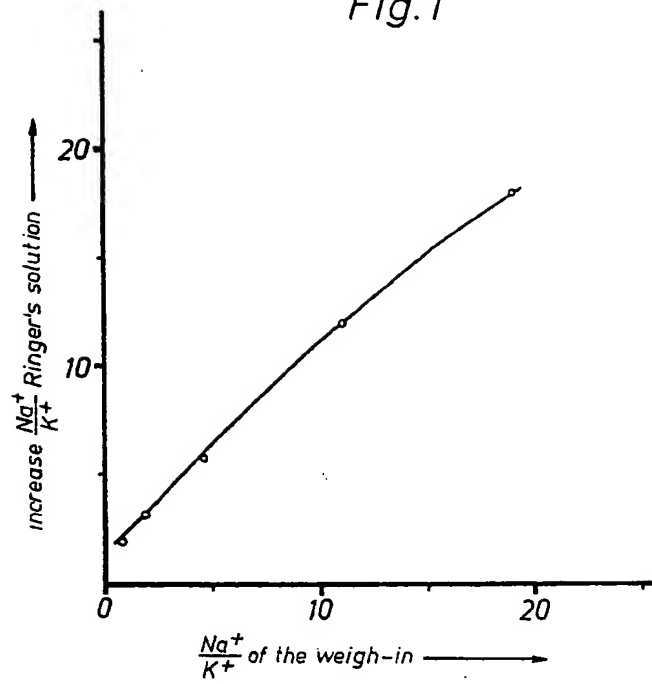


Fig. 2

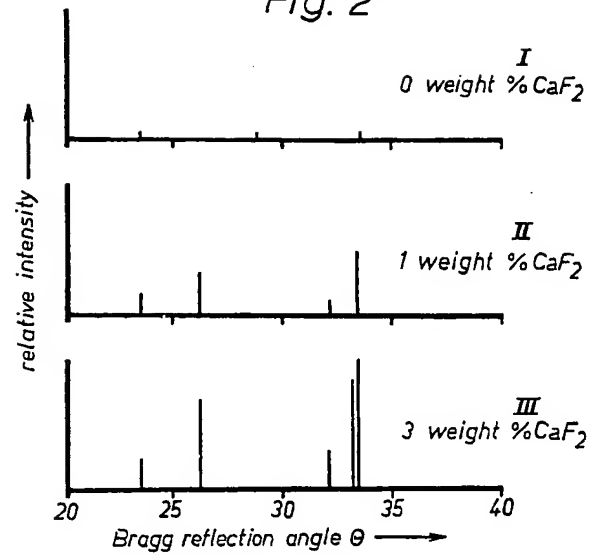
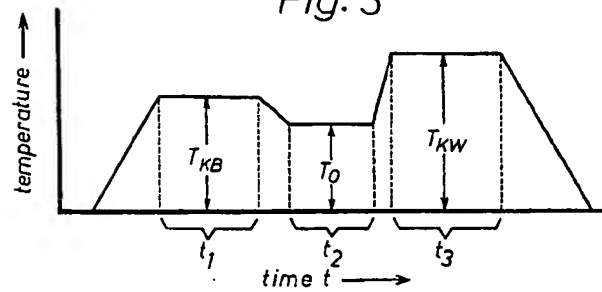


Fig. 3



1441082

COMPLETE SPECIFICATION

3 SHEETS

*This drawing is a reproduction of  
the Original on a reduced scale*

Sheet 3

Fig. 4

